



CASE CO/2-22947/A/PCT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE PCT NATIONAL STAGE APPLICATION OF
CARSTEN SCHELLENBERG ET AL
INTERNATIONAL APPLICATION NO. PCT/EP 04/051980

FILED: SEPTEMBER 1, 2004
FOR: WATER BASED CONCENTRATED

PRODUCT FORMS OF LIGHT
STABILIZERS MADE BY A HETEROPHASE
POLYMERIZATION TECHNIQUE

U.S. APPLICATION NO: 10/570,736
35 USC 371 DATE: MARCH 7, 2006

Group Art Unit: 1713
Examiner: P. D. Mulcahy

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

I, Frank Pirrung, a citizen of Germany and presently residing in Binzen, hereby declare:

That I was awarded the degree of PhD in Organic Chemistry by the University of Amsterdam (Netherlands), in 1995;

That I have been employed by Ciba Specialty Chemicals (formerly CIBA-GEIGY AG), Switzerland, as a Chemist since 2001, and presently hold the position of Group Leader New Polymer Technologies;

That I have been engaged in the Encapsulation of UV Absorbers for Ciba Specialty Chemicals since 2005;

That I am familiar with U.S. Patent Application Serial No. 10/484,357 and have read and understand US Patent 6,214,929;

That the experiments described in the following have been made by me or under my supervision and the evaluation of the results has been done by myself.

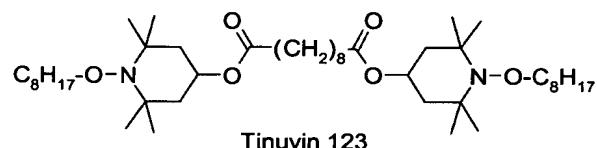
Scope of the Study

The experiments herein are designed to determine whether the addition of non-polar stabilizer to an emulsion of a preformed polymer as disclosed in US 6,214,929 generates the stable, high stabilizer content dispersions of the present invention.

Exact reproduction of the US 6,214,929 examples with the BASF resins exemplified therein is not trivial, as none of the cited materials are readily obtained as samples from the BASF internet, nor is the exact preparation of the resins described in US 6,214,929. It is assumed with great confidence that the resins of these polymer dispersions are made by conventional emulsion polymerization (suspension polymerization) which typically affords particles in the μ -range (1 to 10 μm). The present application however specifically relates to resin particles below 1000 nm, i.e., less than 1 micron. Therefore, in order to provide a direct comparison between appropriately sized particles, polymers are prepared in the experiments below using miniemulsion technology, known to produce resin particles in the sub-micron range, and which are identical, except that in one case they are prepared in the presence of a non-polar light stabilizer.

The experiments therefore compare aqueous emulsions of 60:40 mixtures of a non-polar light stabilizer and a copolymer of methyl methacrylate, methacrylic acid and stearyl methacrylate as carrier resin. In each of the final emulsions prepared below, the copolymer is obtained using the same monomer ratios and reaction conditions except that in one case the light stabilizer is present during polymerization as in the present application, while in the other, the light stabilizer is added after the copolymer is prepared as in US 6,214,929.

Tinuvin 123 was chosen as the non-polar light stabilizer because it is a solvent-free liquid at RT:



Experiments

Preparation of reference dispersion R (according to the present invention)

135.0 g of Tinuvin 123 was dissolved in 81.0 g of methyl methacrylate, 1.8 g of methacrylic acid and 7.2 g of stearyl methacrylate. The weight ratio between the active substance and the monomers corresponds to 60:40. This oil phase was added dropwise to a stirred solution of 9.0 g of lauryl alcohol polyglycol (4) ether sulphate, sodium salt (4% on organic phase), in 204 g of

deionised water. After stirring for 30 min and 20 min of ultrasound treatment (Bandelin Sonoplus, Generator GM 2200, 200 W, 20 kHz, 60% power) a kinetic stable emulsion was obtained.

The emulsion was heated up to 40 °C and the initiator t-butyl hydroperoxide (0.64 g, 70% in H₂O) dissolved in 4 g of deionised water was added and then with continuous stirring at 40 °C by a mechanical stirrer a solution of 0.9 g of sodium hydroxymethanesulfinate dissolved in 6 g of water was added over a period of 1 hour.

The reaction mixture was subsequently stirred at 60 °C for one hour, then cooled to RT and filtered via a 20 µm filter. The resulting dispersion had a particle size D₅₀ of 150 nm (by dynamic light scattering DLS, D_{INT} value).

The isolated yield of the resulting dispersion was ca. 450 g, with a solids content of 51.4 wt% (including polymeric particle and stabilizer). The actives content of the aqueous dispersion was 30wt% of Tinuvin 123.

38.0 g of the above 51.4 wt% solids dispersion was diluted with 12.0 g of deionized water to afford 50.0 g of a stable dispersion as an off-white non-transparent liquid with 39.0 wt% solids content. This is called reference **dispersion R**, see right bottle in Picture 1.

Preparation of polymer without Tinuvin 123 present, dispersion A (empty capsules)

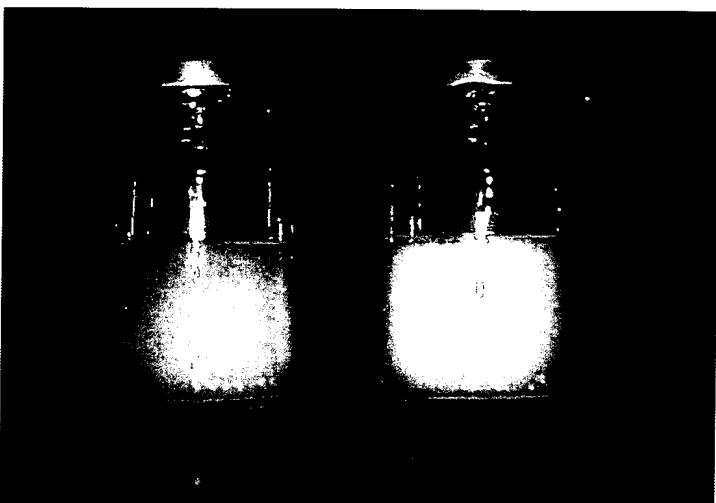
72.0 g of methyl methacrylate, 1.6 g of methacrylic acid and 6.4 g of stearyl methacrylate were added dropwise to a stirred solution of 3.2 g of lauryl alcohol polyglycol (4) ether sulphate, sodium salt (4% on organic phase), in 295 g of deionised water. After stirring for 30 min and 20 min of ultrasound treatment (Bandelin Sonoplus, Generator GM 2200, 200 W, 20 kHz, 60% power) a kinetic stable emulsion was obtained.

The emulsion was heated up to 40 °C and the initiator t-butyl hydroperoxide (0.53 g 70% in H₂O) dissolved in 5 g of deionised water was added and then with continuous stirring at 40 °C by a mechanical stirrer a solution of 0.8 g of sodium hydroxymethanesulfinate dissolved in 15 g of water was added over a period of 1 hour.

The reaction mixture was subsequently stirred at 60 °C for one hour, then cooled to RT and filtered via a 20 µm filter. The resulting particles have a particle size D₅₀ of 40 nm (by DLS).

The isolated yield of the resulting dispersion A was ca. 400 g of a semi-translucent liquid with a solids content of 19.3 wt%, see left bottle in Picture 1. The polymeric particles do not contain

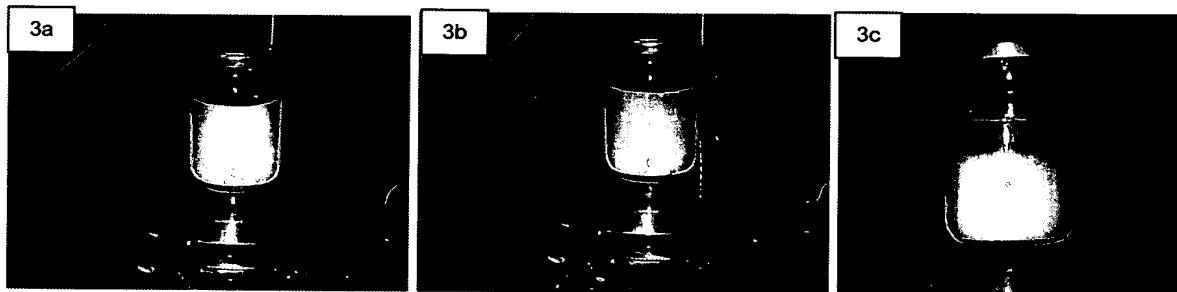
Tinuvin 123 as active substance and are considered empty capsules. The weight ratio of the monomers building up the polymer is identical to that of reference dispersion R.



Picture 1: **dispersion A** on the left, and **dispersion R** on the right

3. Addition of the light stabilizer according to US 6,214,929, dispersion B

To 50.0 g of dispersion A was added 15.0 g of Tinuvin 123, which corresponds to the amount of Tinuvin 123 present as an encapsulated component in 65 g of reference dispersion R, resulting in a two phase system with Tinuvin 123 as a yellowish oil phase on top. As in US 6,214,929, the resulting mixture was stirred for 1 h at room temperature. The sequence of images in Picture 3 shows that no homogenization of the two phases took place under stirring conditions, and oil droplets of Tinuvin 123 separate visually on the vessel walls. The speed of the magnetic stirrer was set at 100 rpm (see vortex formation in Pictures 3a and 3b). Picture 3c shows the result after 1 h of stirring with the separation process in dispersion B almost completed after the movement of the stirrer had been stopped a few instances before.



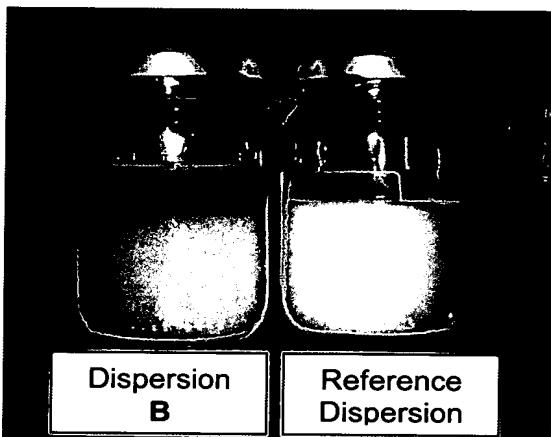
Picture 3: a) at $t = 1$ min, b) at $t = 30$ min, c) at $t = 61$ min.

Thus, addition of Tinuvin 123 to a preformed polymer (otherwise identical to that of dispersion R) under the conditions of US 6,214,929 does not lead to a stable emulsion as in dispersion R.

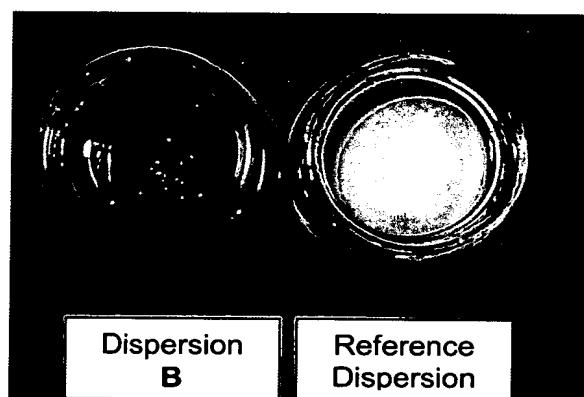
Results and Discussion

Further comparison of dispersion **B** with the dispersion **R** of the present invention reveals:

- the aspect of the aqueous phase in dispersion **B** (lower phase) is still translucent. This is an indication that the size of the dispersion particles did not change. In reference **R** the dispersion is not transparent, due to the larger particle size of the dispersion.
- Measurement of the particle size of aqueous dispersion **B** by DLS confirms this observation. If the empty capsules became filled, the D_{50} value should increase from 40 nm (dispersion **A**, empty capsules) to ca. 150 nm (reference **R**, filled capsules). However, dispersion **B** shows a D_{50} of 41 nm. This is no increase within the error of the determination.
- Measurement of the solid content of the aqueous lower phase in dispersion **B**. If Tinuvin 123 had migrated into the capsules of the aqueous phase, the maximum solids value that can be reached is ca. 39 wt%. However, dispersion **B** shows 19.6 wt% which is within the margin of error of 19.3 wt%, the initial value of dispersion **A**.
- Visual examination of the level of the aqueous layer in dispersion **B** compared with the original level in dispersion **A**, and reference dispersion **R**, i.e. 50 g of dispersion, picture 4, has not changed throughout the experiment, a further indication that only limited migration of Tinuvin 123 from the oil phase into the empty capsules of the water phase could have occurred.



Picture 4: final products (side view) after 5 min



Picture 5: final products (top view)

4. Conclusion

It is clear from the above results that performing a heterophase radical polymerization of ethylenically unsaturated monomers in the presence of a large amount of a non-polar organic light stabilizer, e.g., 100 parts or more of light stabilizer per 100 parts of carrier, results in a different physical entity than adding the stabilizer to an otherwise identical polymer formed in the absence of the stabilizer.

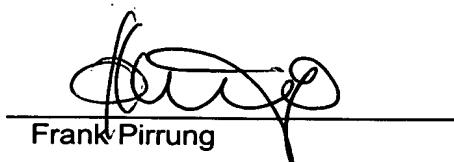
From the above experiments it is concluded that no migration, or at best only limited migration of the non-polar stabilizer occurred into the empty dispersion particles under the conditions described in US 6,214,929 and a two phase system is obtained. Significant differences in the visual and physical aspect of the products are observed.

Thus, while the disclosure of US 6,214,929 may be adequate for the preparation of aqueous resin dispersions containing the lower concentration of certain additives, the disclosure does not allow for the preparation of aqueous resin dispersions containing the high concentration of non-polar additives provided by the present invention. Additionally, the above experiments indicate that one does not obtain a polymer of the instant invention without having the stabilizer present during polymerization.

The considerable increase in the amount of non-polar light stabilizer that can be incorporated into a stable aqueous polymer suspension made possible by the present invention could not be deduced from the existing art. Accordingly, the subject matter of the claims of the present application is clearly novel and non-obvious.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 10 day of March 2008



Frank Purrung